Abstract

Surface modification has wide ranging implications in lubrication, microelectromechanical systems (MEMS), colloidal systems and biological membranes. Surface modification plays an important role in stabilizing gold nanoparticles, which have applications in targeted drug delivery and catalysis. A variety of surface modification techniques are used for controlling corrosion and wettability, as well as used extensively to understand the nature of interactions between surfaces. This thesis is mainly focused on understanding the kinetics, film growth and surface modification by long chain molecules physisorbed on a surface.

The time evolution of film growth and domain formation of octadecylamine on a mica surface is studied using ex-situ AFM and reflectance FTIR. A novel technique of interface creation is developed to measure the height of the adsorbed film. The results show three distinct regions of film growth mechanism. Region I, corresponds to thin film and the interface height is in the monolayer regime. The transient regime (II) consists of a sharp increase in the film thickness, from 1.5 nm to 25 nm within a time span of 180 s. In the final stage of film growth the film thickness is invariant with time, during which domain coarsening is observed. Domain evolution reveals a non-monotonic variation in the domain size as a function of adsorption time. A three stage mechanism is proposed to explain the domain evolution on the surface.

In order to explain the observed film thickness variation, we have developed and tested various models to explain the thin to thick film transition observed in the AFM experiments. A model based on adsorption kinetics is solved to obtain the evolution of the adsorbed film. The model with a two-step adsorption isotherm quantitatively captures the thin to thick film transition observed in the AFM experiments. The statistical thermodynamics of adsorption of long chain molecules on

a surface has been studied using a lattice model. The molecules are characterized by backbone chain, either lying parallel or perpendicular to the surface. A square lattice with nearest neighbour interactions and a mean field approximation are used to generate the adsorption isotherms for different molecules as a function of chain length. The molecules change their orientation from a surface parallel to an upright configuration with an increase in chemical potential. A similar transition (with time) in the molecular orientation has been observed in the AFM experiments. The transition between these two orientations is accompanied by an entropy maximum

The last part of the thesis is concerned with carbon-carbon interactions. More specifically, we are interested in the interactions between graphite surfaces and their modification in the presence of a lubricant or base oil. Diamond like carbon (DLC) AFM tips and highly oriented pyrolitic graphite (HOPG) have been used for this study. Experiments were carried out by treating HOPG graphite in hexadecane oil at different temperatures. It is observed that pull-off forces on bare graphite are smaller when compared to the treated surface. The magnitude of the pull-off forces increases with the temperature of the hexadecane oil bath. Presence of charged patches responsible for the higher adhesion have been confirmed using surface potential microscopy. Results also confirm the presence of a thin liquid-like hexadecane film at room temperature.